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Impact of Argon gas on optical and electrical properties of Carbon thin films

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ABSTRACT

Nanostructured thin films of carbon were synthesized and investigated for their electrical, optical, structural and surface properties. Pulsed Laser Deposition (PLD) technique was used for the preparation of these films under Argon gas environment. A KrF Laser (λ=248 nm) was used as source of ablation and plasma formation. It was observed that the carbon ions and the background gas environment has deep impact on the morphology as well as on the microstructure of the films. Time of Flight (TOF) method was used to determine the energies of the ablated carbon ions. The morphology of film surfaces deposited at various argon pressure was analysed using an atomic force microscope. The Raman spectroscopic measurement reveal that there is shift in phase from sp^3 to sp^2 and a decrease in FWHM of G band, which is a clear indication of enhanced graphitic clusters. The electrical resistivity was also reduced from 85.3×10^{-1} to 2.57×10^{-1} Ω-cm. There is an exponential decrease in band gap E_g of the deposited films from 1.99 to 1.37 eV as a function of argon gas pressure.

1. Introduction

Carbon based compounds and thin films have emerged as exciting smart materials since last two decades [1–3]. Scientist believe that it is a new class of electronic material since the discovery of graphene [4,5]. Carbon compounds at nano scale have potential applications in technology. Pulsed laser deposition (PLD) technique [6,7] has been considered a successful technique for the synthesis of nano materials in the form of thin films. Carbon thin films have wide applications in optics, photovoltaics and electronics [8–10]. Usually, PLD processes are carried out in vacuum by ablation of graphite from a solid state target but the presence of neutral gas during deposition process can significantly influence the surface, structure and stichiometric properties [10,11]. Studies on PLD deposition in inert gas environment have shown that variation in gas pressure of Helium, Argon and Xenon the deposition rate changes [12]. It has also been reported that shifting of DLC to cluster like films has been observed by variation of helium pressure [13]. The impact of background gas has been attributed to a reduction in kinetic energies of expanding laser induced plasma; consequently a complex energy and momentum transfer mechanism with gas atoms take place. To determine the impact of background gas on topological features and structural properties of thin carbon films deposited with PLD and establishing a connection between laser produced plasma and film properties, carbon based films have been deposited on Si substrate in argon gas environment. A visible spectroscopic technique has been employed to establish correlations between plasma interactions with the background gas and film properties. It is proposed that the plasma species and carbon bonds with ambient gas have a deep relationship with respect to plasma ions energy spectrum.

In the present work, thin DLC films were deposited on Si (100) substrate via PLD in an on-axis geometry (vertically aligned). Structural, morphological, electrical and optical characteristics of these graphite films were investigated in relationship with argon pressure and compared with those reported in literature [14,15].

2. Experimental

Carbon thin films were deposited on silicon substrates by employing pulsed laser deposition technique. Ablation of graphite takes place using KrF Excimer laser at an emission wavelength of 248 nm and operated at a frequency of 20 Hz. The laser fluence is calculated as 3.3 J/cm^2 using average spot size. A vacuum chamber was evacuated by a turbo-molecular pump to attain a base pressure of 3×10^{-7} Torr. Argon was used as a background gas during deposition at a base pressure in the range 1-800 mTorr. A single crystal intrinsic silicon substrate (100) is used to deposit thin films of carbon. Substrate was

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cleaned ultrasonically before deposition. A pulsed laser beam was brought to focus on the rotating graphite surface which is mounted on the target holder inside the vacuum chamber. The substrate is placed in front of ablated plasma plume at a distance of 4 cm from the target for the deposition of thin films. A schematic of experimental setup is presented in Fig. 1..

The laser induced ablated species from graphite moved towards the substrate in a forward peaking manner [16] along with interacting Ag atoms on the way and deposited onto substrate in the form of thin film. Plasma species were characterized for ion energies using fast response Faraday cups. The electrical properties of carbon films were investigated using linear four-probe measurements.

3. Results and discussion

3.1. Raman spectroscopic analysis

Raman spectra of films deposited on Si substrates (100) at varying ambient gas pressures are shown in Fig. 2. The instrument uses He-Cd laser as source at a wavelength of 442 nm. The spectra represents two peaks, one centred at approximately 1565 cm^{-1}, and second one at ~1350 cm^{-1}. These two peaks are normally attributed to G and D bands, respectively [17,18]. A peak fitting method (Gaussian profile) is applied to both peak. The obtained results are very much inconsistent with results as observed by other reported carbon films [19,20], which also explored the behavior of sp^2 vs sp^3 hybridization as a function of phosphorus via PLD technique and variation of these fraction via substrate temp variations. In graphite films the G-band is associated with phonons having first-order scattering and being E_{2g2}symmetry. It is the relative vibrations of sp^2 bonded carbon which exist between C=C bonding of conjugated or olefinic carbon. The D-peak is linked with the breathing mode in six-fold aromatic rings with an activated disorder A_{1g}. Usually, D mode does not exist in perfect graphite as reported by A. Hu et.al [21]. The raman spectra in Fig. 2, showed a slight shift to higher wavenumber with the variation in background gas pressure..

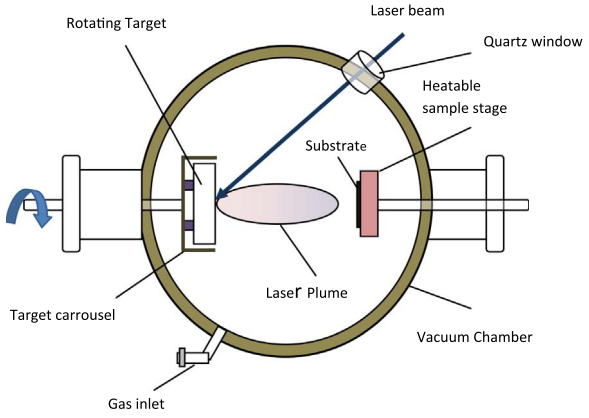

Fig. 1. Schematic diagram of PLD system.

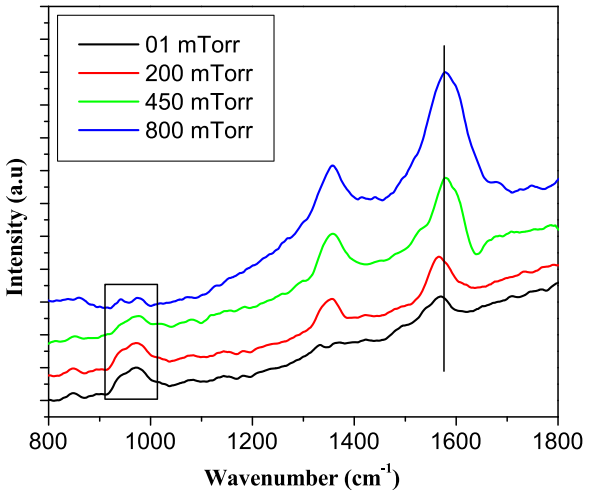

Fig. 2. Raman spectra of DLC films deposited on silicon substrates at different gas pressures.

The structural changes about sp^2 hybridized domains in carbon thin films can be obtained by the ratio (I_D/I_G) of intensities for G and D bands along with the position of G peak. The I_D/I_G ratio decreased with an increase in ambient gas pressure as shown in Fig. 3. Such behavior reveals an increase in the size of the sp^2 domains which in turn reflects an increased graphitic character in the DLC films due to large number of graphite clusters. Raman spectra also help to predict the size and defects of graphite clusters in order to determine the band gap (E_g). It is a well-established fact graphite cluster size is proportional to its band gap [21]. The spectral results show that the D band is growing for the film deposited at higher gas pressure indicating that there is an increase of disorder due to development of large graphitic clusters which are due to phonons associated with the grain boundaries of these clusters, such results are in agreement with the previous work [22,23]. The peaks below 1000 cm^{-1} is due to vibrations from silicon substrate..

3.2. Optical characterization

Optical band gap (E_g) for DLC films was determined using SE technique by employing Cauchy model [24]. It uses absorption (α) and extinction coefficient (k) through the relation;

$$\alpha = 4\pi\ k/\lambda \quad (1)$$

where λ is the wavelength of incident beam. The optical band gap can be estimated using Tauc-plot by utilizing the absorption coefficient. The relationship can be expressed through the relation [25]:

$$\alpha = (B/h\upsilon)\{h\upsilon - E_g\}^n \quad (2)$$

where B is material's constant and hυ is the energy of photon, E_g is bandgap. The exponent n is theoretically bound to direct and indirect electronic transitions. In Tauc plot photon energy (hυ) was plotted vs $(\alpha h\upsilon)^2$ for each individual sample. E_g can be estimated by the intercept of the extrapolated linear fit at α=0 on the Tauc plot curve.

Fig. 4, shows the relationship of band gap E_g of the deposited thin DLC films with respect to variation in Argon gas pressure. By applying least square fit to the Tauc plot results an exponential fit which reveals that E_g decreases exponentially from 1.99 to 1.37 eV. Present results are very much consistent with other reported laser plasma deposited DLC thin films [26–28]. As the gas pressure increases the chance of

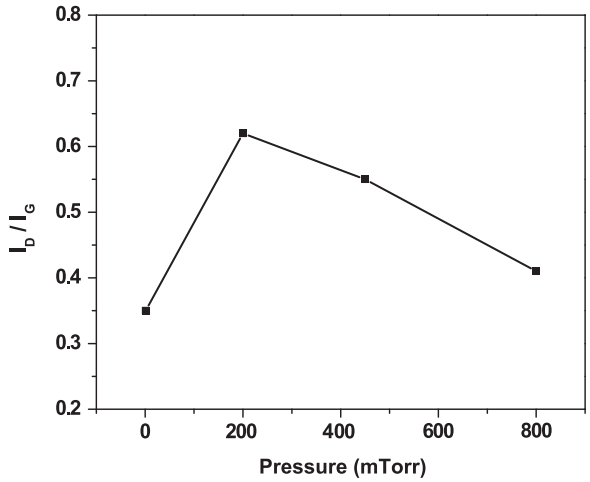

Fig. 3. I_D/I_G ratio of the films deposited at different gas pressures..